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Dramatic solvent effect on the volume of the Diels-Alder reaction between tetracyanoethylene and cyclopentadiene

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Abstract

The partial molar volumes (V) and the enthalpies of dissolution (ΔdisH) for tetracyanoethylene, cyclopentadiene, and their Diels-Alder adduct were determined at 25 °C. Eleven solvents of the π and n-donor type were used. The use of alkylbenzenes as solvents for tetracyanoethylene induces pronounced changes in the enthalpy of dissolution (up to 26 kJ mol-1) and in the partial molar volume (up to 11 cm3mol-1), whereas these parameters for the adduct change slightly. The V and ΔdisH values for cyclopentadiene virtually do not depend on the nature of the solvent. In the case of tetracyanoethylene and the adduct in n-donor solvents, considerable variations of the v and ΔdisH values are observed; they are not linear functions of the change in the partial molar volume of the adduct. Therefore, the reaction volumes in acetonitrile (-40.69) and ethyl acetate (-45.56) differ sharply from those in o-xylene (-24.28) and mesitylene (-21.76 cm3mol-1).

Keywords

Diels-Alder reaction, Partial molar volume, Reaction volume, Specific interactions, Tetracyanoethylene